

Crystal Structure and Magnetic Properties of Pyrrhotite-Type Compounds $\text{Fe}_{7-y}\text{V}_y\text{S}_8$

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The pyrrhotite-type compounds $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ have been synthesized and studied by means of the X-ray diffraction and magnetization measurements in order to reveal how the substitution of V for Fe affects the crystal structure, phase transition and magnetic properties. The growth of the V content in $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ results in changes of the crystal structure and leads to a sharp decrease in the resultant magnetization, non-monotonous change of the coercive field and reduction of the magnetic ordering temperature. Unlike ferrimagnetic ordering in pyrrhotite Fe_7S_8 the compound V_7S_8 is observed to exhibit a Pauli-paramagnetic behaviour.

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1. Introduction

Pyrrhotite (Fe_7S_8) consists of completely filled layers of chalcogen sandwiched between Fe layers one of which is full, while another one contains vacancies [1]. The Fe magnetic moments ($\mu_{\text{Fe}} \sim 3.2\mu_{\text{B}}$) are arranged parallel to each other inside each layer, but are coupled antiparallel to each other between successive layers [2]. The presence of vacancies in every second Fe layer leads to incomplete compensation of magnetic moments and to a ferrimagnetic order which enters below the Neel temperature of about 590 K [1,2]. The magnetic properties of Fe_7X_8 are strongly influenced by substitutions in both the Fe [3, 4] and chalcogen sublattices [5]. The replacement of iron in $\text{Fe}_{7-y}\text{M}_y\text{X}_8$ ($\text{X} = \text{S}, \text{Se}$) by other 3d metal ($\text{M} = \text{Ti}, \text{Co}$) atoms in cation layers is found to be non-random and dramatically affects the magnetic behavior [4]. The cation partitioning between layers in pyrrhotite-type compounds is observed to depend on the kind of substituting M atoms assumingly owing to the difference in the spatial extension of 3d orbitals [4]. In order to confirm this suggestion further the present work aims to study how the substitution of V for Fe affects the properties of the $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ compounds.

2. Experimental

Polycrystalline samples $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ ($y = 0-7$) were obtained by solid-state reactions in evacuated quartz tubes. The starting materials were small vanadium pieces (99.9% purity), sulfur (99.99%) and powder of iron (99.98%). The method of synthesis of $\text{Fe}_{7-y}\text{M}_y\text{S}_8$ samples has already been described in detail [4]. In order to examine the quality of the samples and the changes in the crystal structure upon substitution a powder X-ray

diffractometer Bruker D8 ADVANCE with Cu $K\alpha$ radiation was used. The measurements of the magnetic susceptibility and magnetization were performed by means of a Quantum Design SQUID MPMS magnetometer and Vibrating sample magnetometer Lake Shore VSM 7407.

3. Results

According to X-ray diffraction all the synthesized samples $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ ($0 \leq y \leq 7$) have layered superstructures of the NiAs-type, while in the case of Ti for Fe substitution, the single phase $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$ samples were obtained only at $y \leq 4$ [3]. The changes in the crystal structure in $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ with substitution can be characterized by the lattice parameters a_0 and c_0 of the NiAs fundamental unit cell. The V for Fe substitution is found to result in the growth of the c_0 value from 5.668(6) Å in Fe_7S_8 ($y = 0$) up to 5.789(2) Å in V_7S_8 ($y = 7$), however, the average intra-layer distance characterized by lattice parameter a_0 slightly decreases with increasing V content from 3.436(1) Å for $y = 0$ down to 3.376(3) Å for $y = 7$.

The unit cell volume remains almost unchanged upon substitution in the $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ system.

The replacement of Fe by V atoms is observed to dramatically affect the magnetization behaviour in magnetic fields (shown in Fig. 1). As in the case of the Ti for Fe substitution [3, 4], the replacement of Fe by V up to $y = 1$ significantly reduces the magnetization, while further growth of the V content results in a non-monotonous change of the magnetization. Fig. 2a shows the concentration dependence of the magnetization M_{50} measured in a field of 50 kOe at temperature 2 K on the $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ samples. The non-monotonous behaviour of the magnetization was also observed in the $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$ system, which was explained by the ferrimagnetic ordering of the Fe magnetic moments and by non-random substitutions in the cation layers [3, 4] since the statistical distribution of substituting atoms should result in the monotonous reduction of the resultant magnetization.

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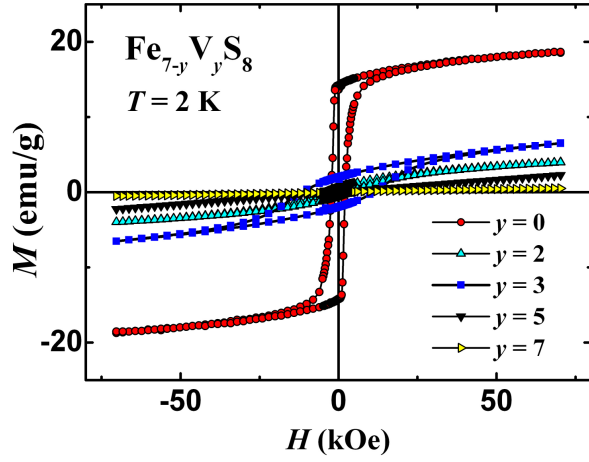


Fig. 1. Field dependences of the magnetization measured at $T = 2$ K on the $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ samples.

For $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$, the non-random Ti for Fe substitution in alternating cationic layers was derived from neutron diffraction data [4]. The presence of a minimum of the resultant magnetization at $y \sim 1.5$ in $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ may be associated with the compensation of the sublattice magnetizations, as in $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$ [3, 4]. However, unlike the $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$ samples with $y > 1.5$ exhibiting almost in twice increased magnetization in high magnetic fields in comparison with the non-substituted Fe_7S_8 compound, all the $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ compounds demonstrate substantially lower values of the resultant magnetization. There are several origins which may lead to reduced values of the magnetization in the V-substituted compounds: i) the less pronounced partitioning of Fe and V between adjacent layers; ii) the more random distribution of vacancies in all cationic layers and iii) presence of a non-zero magnetic moment on V ions unlike Ti. The neutron diffraction measurements are needed in order to reveal the main factors determining the magnetization behavior with increasing V content in $\text{Fe}_{7-y}\text{V}_y\text{S}_8$.

As follows from Fig. 2b, the substitution of V for Fe in $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ leads to the non-monotonous variations of the coercive field (H_c), as in $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$. The growth of H_c around $y = 1-1.5$ in both the V- and Ti-containing compounds apparently originates in the reduced values of magnetization. Such a behavior is analogous to that observed in vicinity of the compensation temperature in ferrimagnetic materials. When the V content increases up to $y = 3$, the hysteresis loop becomes broader and H_c reaches a value about of 11.5 kOe; further substitution of V for Fe reduces the hysteresis and leads to the paramagnetic behavior of $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ at $y > 6$.

The magnetic state of the V-substituted compounds $\text{Fe}_{7-y}\text{V}_y\text{S}_8$ with $y \sim 5$ seems to be non-homogeneous. The temperature dependence of the magnetic susceptibility of $\text{Fe}_2\text{V}_5\text{S}_8$ (Fig. 3a) shows a remarkable hysteresis at low temperatures when the measurements were made on a sample cooled in zero field (ZFC) or on a sample cooled in an applied field (FC).

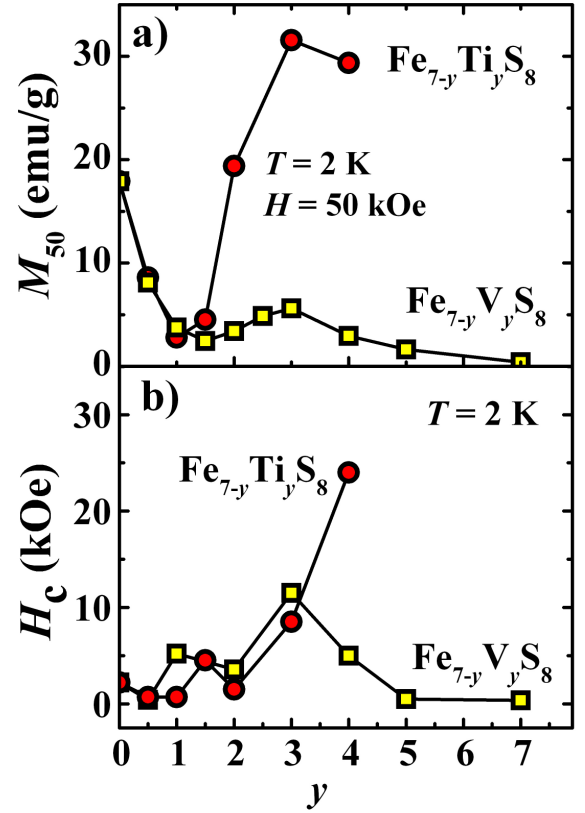


Fig. 2. Magnetization (a) in a field of 50 kOe and coercive field (b) for $\text{Fe}_{7-y}\text{M}_y\text{S}_8$ ($M = \text{V}, \text{Ti}$) at $T = 2$ K as functions of the substituting atom concentrations. The data for $\text{Fe}_{7-y}\text{Ti}_y\text{S}_8$ are taken from Ref. [4].

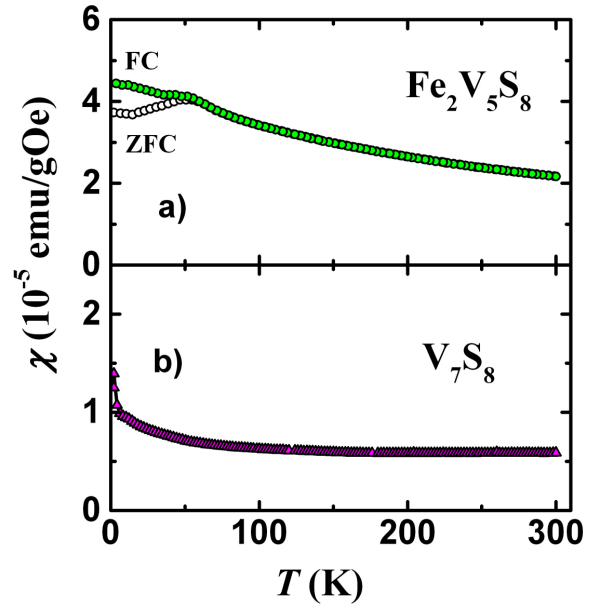


Fig. 3. Temperature dependences of the magnetic susceptibility for $\text{Fe}_2\text{V}_5\text{S}_8$ (a) and V_7S_8 (b) measured at $H = 1$ kOe.

These data together with a reduced magnetization and broad hysteresis loop allow us to characterize the magnetic state of this compound as of cluster glass-type with freezing of the ferrimagnetic clusters below 50 K. As follows from Fig. 3b, the magnetic susceptibility of V_7S_8 ($y = 7$) shows weak temperature dependence above $T \sim 100$ K and a low-temperature upturn of the Curie-Weiss (CW) type. Such a paramagnetic behavior of this compound is consistent with previously reported data for the vanadium sulfides with nearly equiatomic compositions [6]. The $\chi(T)$ dependence for V_7S_8 can be fitted to the expression: $\chi(T) = \chi_0 + C/(T - \Theta_p)$, in which the first term is the temperature-independent Pauli paramagnetic contribution from conduction electrons and the second one is the CW contribution from localized magnetic moments. From the Curie constant C , the effective magnetic moment μ_{eff} was estimated to be $0.3 \mu_B$ per V ion, which is substantially lower than the spin-only values for V^{3+} ($2.83\mu_B$) and V^{4+} ($1.73\mu_B$).

Figure 4 shows the variation of the magnetic ordering temperature (T_N) with the V for Fe substitution in $Fe_{7-y}V_yS_8$ together with the $T_N(y)$ dependence for $Fe_{7-y}Ti_yS_8$. The Neel temperatures for the V-containing samples at $y < 4$ are found to be greater than that for the compounds $Fe_{7-y}Ti_yS_8$ with the same concentrations of the substituting elements.

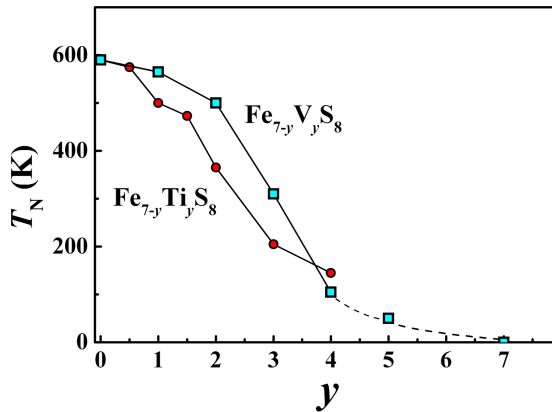


Fig. 4. The concentration dependences of the Neel temperature for $Fe_{7-y}M_yS_8$ ($M = V, Ti$). The data for $Fe_{7-y}Ti_yS_8$ are taken from Ref. [4].

The enhancement of magnetic ordering temperatures in the $Fe_{7-y}V_yS_8$ system may be indicative of the presence of a local magnetic moment on vanadium atoms in the compounds $Fe_{7-y}V_yS_8$ with $y < 4$ in contrast to the titanium atoms in $Fe_{7-y}Ti_yS_8$.

4. Conclusions

The compounds $Fe_{7-y}V_yS_8$ are found to exhibit the layered crystal structures of the NiAs-type in the whole concentration range. The growth of the V content increases the average inter-layer distance and reduces the average intra-layer distance, however, the unit cell volume remains almost unchanged upon substitution. The

replacement of Fe by V in $Fe_{7-y}V_yS_8$ having a ferrimagnetic order at $y = 0$ leads to a non-monotonous change of the resultant magnetization. A minimum of the magnetization around $y = 1.5$ is attributed to the partial compensation of the antiferromagnetically ordered magnetic moments of 3d metal ions located in neighbor cationic layers because of non-random substitutions of V for Fe. The presence of such a minimum indicates that vanadium preferably substitutes iron in layers without vacancies when the V content increases up to $y = 1.5$ as was observed earlier in the case of Ti for Fe substitution [4]. In $Fe_{7-y}V_yS_8$, the coercive field reaches a maximal value 11.5 kOe at $y = 1.5$ obviously because of a reduced value of the resultant magnetization at this concentration. Unlike a non-monotonous variation of the resultant magnetization and coercive field the growth of the V content leads to a monotonous decrease of the magnetic ordering temperature. The $Fe_{7-y}V_yS_8$ compounds are observed to exhibit a cluster-glass behavior within the concentration range $4 < y \leq 6$. A reduced value of the effective magnetic moment per V atom in V_7S_8 ($\mu_{eff} = 0.3 \mu_B$) indicates that the magnetic state of this compound can not be described in terms of a model with localized d electrons. The 3d electrons of V ions in the $Fe_{7-y}V_yS_8$ system are rather in an intermediate regime between strongly localized and itinerant case.

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